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PROPERTIES OF THERMOSHRINKED FILMS BASED ON POLYVINYLCHLORIDE

Dependence of thermal shrinkage of films based on polyvinylchloride (PVC) on temperature is established. The technique of determining PVC film shrinkage speed within a wide interval of temperatures is developed. The effect of the content of the plasticizer and heat treatment on the physico-mechanical parameters of PVC films is shown. The influence of the duration of mixing the components of the mix on physico-mechanical parameters of PVC films is established. Linear equations of regression of temperature rise kinetics in the course of mixing the ingredients in a high-speed agitator and those of subsequent kinetics of cooling the mix at mixing are obtained.

Introduction. Thermoshrinked PVC films are widely used for packaging. These films are durable, transparent and light-permeable. Therefore the study of properties of such films and fields of their application present some practical interest.

The aim of the investigation is to study thermal shrinkage and elastic-durable parameters of PVC films produced in amalgamation "Don-Polymer" (Voronezh) and the influence of operating conditions for mix preparation on these parameters.

Main part. 1. *Study of thermal shrinkage properties of films.* Definition of PVC film thermal shrinkage speed presents practical interest.

Definition of the maximal shrinkage of polyethylene (PE) films is stated in State Standard 25951-83. There are no techniques on determining the kinetics of PE, PVC film thermal shrinkage. That's why the first stage of our investigation was devoted to: development of the technique for assessing the shrinkage speed of films of various nature; determination of the temperature for instant shrinkage; establishment of the minimal temperature boundary for thermal shrinkage development.

For the purpose of testing we cut the samples along and across the direction of film extrusion. The bath was filled with a heat reagent (water – for PVC, cellular silicone – for PE) which was heated to the required temperature. The samples under analysis were cured in the reagent under various duration of dipping, then they were pulled out and cooled; the residues of the heat reagent were removed from the film surface with the help of filtrating paper. After that the dimensions were determined and shrinkage was calculated. Dependences of the degree of film shrinkage on the temperature and time duration of thermal treatment were determined by the kinetics of PVC film thermal shrinkage within the temperature interval 60–100°C in hot water and that of PE films within the temperature interval 130–145°C in cellular silicone.

It was shown that the film shrinkage kinetics was described by a broken line tentatively divided into two zones of thermal shrinkage: I – fast; II – slow. There is an assumption: the boundary between zones I and II of thermal shrinkage is the duration providing 90% film shrinkage from its maximum value. So, shrinkage was described by two linear equations:

$$y_1 = c_1 \cdot x - \text{zone I,} \\ y_2 = c_2 \cdot x + d_2 - \text{zone II.}$$

Assessment of the film shrinkage speed in zone I and II was made on coefficients c_1 and c_2 (Tables 1–2). Decrease of the temperature of film thermal shrinkage changed the shape of the broken line. The speed in zone I of fast shrinkage decreases (direct line became more sloping). With increase of temperature the thermal shrinkage speed increased. It was established that the maximum speed of fast thermal shrinkage (Table 1) depended on the total content of plastifiers in the formulations. For example, the maximum speed of fast thermal shrinkage of formulations GU-V, DP-1 began at 80°C. Deceleration of thermal shrinkage in zone I for formulation DPK-120 along the film extrusion in comparison with formulation DPK-90 is explained by the plasticizer volatilization from the hot tubing of the last formulation in the process of extrusion.

In accordance with the data given in Table 3 we obtained the calculated duration (x_{gr}) of fast thermal shrinkage of PVC films of the type

$$x_{gr} = d_2 / (c - c_2).$$

It is shown that for all formulations the maximum speed of thermal shrinkage (minimal time duration of fast thermal shrinkage) was observed at 75–80°C. It is established that development of visible (minimal boundary of development) thermal shrinkage of films is observed beginning from 60°C.

Table 1

Effect of temperature, formulation, tubing extrusion direction on fast shrinkage speed (c_1) of PVC films in zone I

Code of formulation	Shrinkage temperature						Tubing extrusion direction
	60°C	65°C	70°C	75°C	80°C	100°C	
DPK-120	0.1	3.1	5.5	∞	∞	∞	Across
DPK-90	0.2	1.7	20.0	∞	∞	∞	
UPK-V	3.2	8.4	11.7	36.0	36.0	∞	
GU-V	1.4	14.4	∞	∞	∞	∞	
DP-1	4.8	32.0	∞	∞	∞	∞	
DPK-120	0.1	0.1	3.1	9.3	20.4	∞	Along
DPK-90	0.1	0.8	8.5	∞	∞	∞	
UPK-V	0.8	1.0	19.6	15.3	22.0	∞	
GU-V	0.5	1.6	10.1	17	∞	∞	
DP-1	0.2	7.7	9.0	34.0	36.0	∞	

Table 2

Effect of temperature, formulation, tubing extrusion direction on speed of slow shrinkage (c_2) of PVC films in zone II

Code of formulation	Shrinkage temperature												Tubing extrusion direction
	60°C		65°C		70°C		75°C		80°C		100°C		
	c ₂	d ₂	c ₂	d ₂	c ₂	d ₂	c ₂	d ₂	c ₂	d ₂	c ₂	d ₂	
DPK-120	0.02	28.7	0.06	33.3	0.1	34.7	0.6	33.4	—	33.0	0	36.0	Across
DPK-90	1.30	−6.9	0.06	29.8	0.8	30.2	0.6	33.4	1.0	31.4	0	36.0	
UPK-V	−0.12	44.8	−0.06	41.6	0.9	5.5	−0.8	42.8	0.6	37.4	0	42.0	
GU-V	−0.24	33.8	1.00	22.7	—	28.0	0.8	25.6	1.0	25.0	0	28.0	
DP-1	−0.04	40.9	1.60	32.4	−0.6	38.6	0.6	39.4	0.6	39.4	0	38.0	
DPK-120	0.02	29.7	0.02	30.3	0.1	35.6	—	38.0	—	38.0	0	40.0	Along
DPK-90	0.02	29.7	0.10	29.7	0.1	34.2	—	36.0	1.4	31.0	0	40.0	
UPK-V	—	38.0	0.10	31.3	1.0	35.3	1.0	0.9	1.0	34.7	0	42.0	
GU-V	0.02	37.7	0.05	39.2	0.1	40.8	1.0	1.0	—	42.0	0	46.0	
DP-1	0.03	27.5	0.02	37.2	1.5	21.8	—	38.0	0.8	36.2	0	40.0	

Table 3

Calculated duration (x_{gr} , c) of PVC film fast thermoshrinkage completion in zone I

Code of formulation	Shrinkage temperature						Maximal shrinkage, %	Tubing extrusion direction
	60°C	65°C	70°C	75°C	80°C	100°C		
DPK-120	359.0	11.0	6.4	0	0	0	32	Across
DPK-90	6.3*	18.1	6.4	0	0	0	32	
UPK-V	14.0	4.9	0.5*	1.2	1.1	0	38	
GU-V	21.0	1.7	0	0	0	0	26	
DP-1	8.5	1.1	0	0	0	0	34	
DPK-120	371.0	378.8	11.7	0	0	0	36	Along
DPK-90	371.0	42.4	4.1	0	0	0	36	
UPK-V	48.0	34.8	1.9	0.1*	1.7	0	38	
GU-V	126.0	25.3	4.1	0.1	0	0	41	
DP-1	161.8	4.8	2.9	1.1	1.0	0	37	

* Approximate measurements.

The effect of the plasticizer content on the temperature boundary of thermal shrinkage development was revealed. Thus, formulations DPK-120 and DPK-90 with the total plasticizer content 5.9 wt % the duration of vivid thermal shrinkage at 60°C was

359–371 s, and for formulations UPK-V with the total plasticizer content 12.4 wt % – 14–18 s.

For formulation GU-V the duration of vivid thermal shrinkage along and across the tubing was 21 and 126 s, respectively. This difference is

explained by stronger initial extrusion of the film (across – 26%, along – 41%).

Therefore, the total content of plasticizers (DOF, DINF, ESM) lowered the temperature boundary of vivid thermal shrinkage development, shortened the time duration of film thermal shrinkage and, thus, made the ensured time of their storage shorter.

Assessment of PE film shrinkage speed in zones I and II of thermal shrinkage at various temperatures was made on the basis of coefficients c_1 и c_2 (Table 4).

In accordance with the data, indicated in Table 5, there was established a calculated duration of fast thermal shrinkage completion for PE films. It is shown that instant thermal shrinkage (minimal duration of thermal shrinkage) began at 140°C. It is established that the temperature boundary of film visible thermal shrinkage development is observed beginning from 130°C.

Thus, the recommended working temperature of PVC film thermoshrinkage was equal to 75°C, for PE films it was 140°C, and the ensured time of storage for PE films exceeded the one for plastified PVC films.

2. *Study of elasticity and durability of films.* We investigated physico-mechanical properties of PVC films with various content of plasticizers before and after thermal shrinkage along and across the extrusion direction.

In accordance with the data, indicated in Table 6, relative elongation at rupture (E_r) of initial films before shrinkage across the tubing extrusion direction was 0–9% and along it – 0–6%. Development of high values E_r for individual formulations pointed to the increased content of plasticizers in their composition (formulations GU-V, DP-1 in comparison with formulation UPK-V).

Table 4
Effect of temperature and tubing extrusion direction on the speed of fast (c_1 , zone I) and slow (c_2 , zone II) shrinkage of PE film

Shrinkage temperature								Tubing extrusion direction
130°C		135°C		140°C		145°C		
c_1		c_1		c_1		c_1		
2.7		1.2		∞		∞		
7.7		9.9		∞		∞		Across
Along								
c_2	d_2	c_2	d_2	c_2	d_2	c_2	d_2	
0.2	27.7	0.32	28.8	0.24	32.2	0.4	32.8	Across
0.3	51.3	0.3	54.7	0.6	53.9	3.0	47	Along

Table 5
Calculated duration (x_{gr} , c) of PE film fast thermoshrinkage completion in zone I

Shrinkage temperature				Maximal shrinkage, %	Tubing extrusion direction
130°C	135°C	140°C	145°C		
11.1	32.7*	0	0	30	Across
6.9	5.7	0	0	50	Along

* Approximate measurements.

Table 6
Physico-mechanical parameters of PVC and PE films along and across tubing extrusion direction before and after thermoshrinkage

Code of formulation	Maximal shrinkage, %		Without preliminary shrinkage				With preliminary shrinkage			
	across	along	f_r , MPa, across	E_r , %	f_r , MPa, along	E_r , %	f_r , MPa, across	E_r , %	f_r , MPa, along	E_r , %
PVC films										
DPK-120	32	36	45.3	7	21.7	1	69.7	0	67.2	0
DPK-90	32	36	39.2	0	39.2	0	16.1	0	29.9	0
UPK-V	38	38	23.5	0	32.0	1	60.6	0	37.2	0
GU-V	26	41	27.8	6	63.7	6	63.0	0	52.8	0
DP-1	34	37	57.8	9	64.5	5	68.8	0	64.6	0
PE film										
Terminal (40 microns)	28	50	30.3	800	27.0	600	28.1	21	29.3	33

Thermal shrinkage of films (180°C, 30 s) resulted in the loss of E_p for all formulations. This was explained by volatilization of a part of the plasticizer which is indirectly called the acetone extract of film samples (Table 7). Thus, the acetone extract for formulations GU-V, DP-1 before thermoshrinkage was –31.5 and –9.7 wt % and after thermoshrinkage it was –15.0 and –8.6 wt %, respectively.

There were determined differences (anisotropy) in durability for all formulations across and along the film tubing extrusion direction. Durability at rupture (f_r) of films of all formulations before shrinkage across extrusion direction was 23.5–57.8 MPa, and along it – 21.7–64.5 MPa.

It is discovered that thermal shrinkage of films changed their durability. For all formulations, except formulation DPK-90, durability, as a rule, increased. This was accounted for by volatilization of a part of the plasticizer and development of the effect of antiplastification. Formulation DPK-90 revealed abnormal decrease of film durability after shrinkage from 39.2 to 16.1–29.9 MPa. It is connected with high volatilization of the plasticizer due to an insufficient duration of mixing the plasticizers with PVC resin indirectly determined by the temperature of completing the mixing process (formulation DPK-90 – heating to 90°C, formulation DPK-120 – to 120°C). Formulation DPK-90 revealed larger loss of plasticizers at extrusion in comparison with DPK-120. The acetone extract of DPK-120 and DPK-90 was 21.6 and 14.4 wt %, respectively (Table 7).

In their turn, thermoshranked PE films in comparison with PVC films preserved durability in the interval from 28.1 to 29.3 MPa, but they lost E_r from 600–800 to 21–33%.

3. *Study of regimes of PVC film ingredients mixing.* There was investigated the effect of the regime of ingredient mixing on engineering parameters of PVC films. Kinetics of the temperature rise in the course of ingredient mixing and subsequent kinetics of cooling the mix were analyzed on the example of formulation DPK-90.

The order of mixing was the following. At first free-flowing bulk materials (PVC C7056M, thermostabilizers etc.) were loaded into a hot agitator (30°C), the stirrer with rotation 640 rev/min was switched on. At the temperature rise to 40–50°C liquid ingredients (plasticizers, epoxidated soya bean oil etc.) were loaded. The process of mixing lasted in the first case up to temperature 90°C (formulation DPK-90), and in the second one – up to 120°C (formulation DPK-120). Then the hot mix was unloaded into a cooling chamber with a stirrer. Further, the cooled mix was screened through a vibrosieve and subjected to ageing during 12–48 hours. In the end, using the extrusion-blown method we obtained films in the form of tubings which were cured in the bath with hot water (83°C) and subjected to two-axis extrusion.

The temperature in the extruder zones was: 1 – 165–166°C; 2 – 165–193°C; 3 – 201°C. The temperature of the head was 201°C. The number of revolutions of the main driver was 32 rev/min under the load of current 10.6–10.7 A.

The kinetics of temperature rise in the course of mixing the ingredients was described by linear equations of the type

$$y = a_{11} \cdot x + b_{11} \text{ and } y = a_{12} \cdot x + b_{12}.$$

The speed of temperature rise of the mix a_{11} , a_{12} was 0.2°C/sec (Table 8), and coefficients b_{11} and b_{12} characterized the initial temperature in the mixing chamber in the moment of free-flowing bulk ingredients loading which was equal to 30 and 36°C, respectively.

The kinetics of cooling the mix was also described by the linear equation (Table 8)

$$y = a_{21} \cdot x + b_{21} \text{ and } y = a_{22} \cdot x + b_{22}.$$

The speed of cooling the mix a_{21} , a_{22} was –0.1°C/s and coefficients b_{21} , b_{22} pointed to the initial temperature of the mix in the cooling chamber (for formulation DPK-90 – 80°C and for formulation DPK-120 – 110°C), which indicates that it is 10°C lower than the final temperature in the chamber of hot mixing (90°C and 120°C, respectively).

Table 7

Degree of swelling and acetone extract of PVC films of various formulations

Code of formulation	Thickness, mm	Degree of swelling, %	Acetone extract, wt %
Before thermoshrinkage			
DPK-120	0.04	6.5	–21.6
DPK-90	0.04	8.9	–14.4
UPK-V	0.04	47.8	–14.6
GU-V	0.04	6.6	–31.5
DP-1	0.22	3.0	–9.7
After thermoshrinkage (180°C, 30 s)			
DPK-120	0.11	25.9	–6.9
DPK-90	0.11	29.4	–6.8
UPK-V	0.16	29.3	–11.4
GU-V	0.15	5.6	–15.0
DP-1	0.12	6.7	–8.6

Table 8

Coefficients of regression of temperature change kinetics at ingredient mixing and mix cooling

Ingredient mixing				Mix cooling			
DPK-90		DPK-120		DPK-90		DPK-120	
a_{11}	b_{11}	a_{12}	b_{12}	a_{21}	b_{21}	a_{22}	b_{22}
0.2	30	0.2	36	-0.1	80	-0.1	110

Under the regime of mixing up to temperature 90°C its duration was 300 sec and the time of cooling to terminal temperature 45°C – 340 s, and under the regime of mixing up to temperature 120°C – 510 and 510 s, respectively. Thus, the overall duration of the cycle *heating – cooling* in the first case was 640 s, and in the second – 1,020 s, i. e. 60% longer.

Other formulations were obtained under the regime of mixing in the chamber at 90°C.

Conclusion. While analyzing thermoshrinkage properties of PVC films we developed the technique of determining the film shrinkage speed within a wide interval of temperatures. In analyzing the kinetics of thermoshrinkage we revealed two zones: 1 – fast shrinkage; 2 – slow shrinkage. The kinetics of the first and second shrinkages were described by linear dependence of thermal shrinkage on the duration of thermotreatment. The speed of film shrinkage at various temperatures was assessed on the coefficients of the obtained equations of regression. The overall content of plasticizers in the formulation also effected the speed of film shrinkage. Duration of fast thermoshrinkage decreased with increase of the number of plasticizers.

The optimal temperatures of shrinkage were found: for PVC films – 75°C and for PE films – 140°C. The minimal boundary of thermoshrinkage

development was established (for all PVC film formulations it was 60°C, and for PE film formulations – 130°C).

Physico-mechanical properties of films before and after thermoshrinkage along and across extrusion were studied. It was established that relative elongation at rupture along and across the tubing extrusion before thermal shrinkage was 0–6 and 0–9%, respectively. After thermal shrinkage relative elongation at rupture for all formulations wasn't observed. There were established differences (anisotropy) in durability of films along and across the tubing extrusion direction.

There were obtained linear equations of regression of temperature rise kinetics in the course of mixing the ingredients in the high-rotation agitator and subsequent kinetics of cooling the mix at mixing. Both the kinetics are described by linear dependences. It was discovered that the duration of the cycle of ingredient mixing up to temperature 90°C with subsequent cooling was 60% shorter than the one for mixing up to temperature 120°C with subsequent cooling.

Thus, in the course of investigation the technology of mixing the ingredients for PVC films was analyzed and differences in engineering and performance properties of thermoshranked films based on PVC and PE were determined.

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